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	For	Number Filed		Number Extra		Rate			
Extra Claims	Total Claims	17	-20	0	x	\$	18	= \$	
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- ☒ Applicants hereby claim priority to the provisional application having a priority date of 3/30/99, which application is being converted to a provisional application by petition which is being filed concurrently on 3/14/00 based on nonprovisional Application Serial No. 09/280,510 filed on 3/30/99.

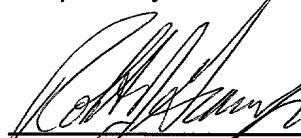
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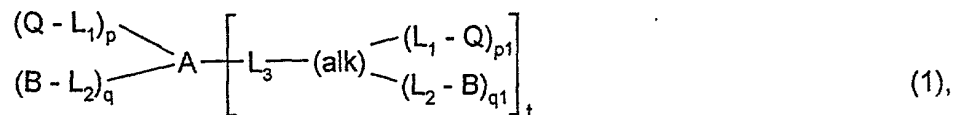
Organic Compounds

The present invention relates to novel crosslinkable copolymers, to a process for the preparation thereof and to the use thereof for the manufacture of moldings, especially ophthalmic moldings.

- 5 U.S. patents Nos. 5,760,100 or 5,807,944 disclose crosslinkable amphiphilic block copolymers comprising a hydrophobic middle block to which are linked two or more hydrophilic blocks. While the materials disclosed therein have proven to be very effective as bulk material for the manufacture of biomedical articles, in particular ophthalmic moldings, their surface properties, in particular the wettability characteristics, are in general not sufficient to use them as a biomedical device without previously applying a suitable coating on their surface.

Therefore, there is a need to provide polymeric materials which may be used for the manufacture of biomedical articles such as ophthalmic moldings per se without a subsequent surface modification. Surprisingly, it now has been found that articles, particularly biomedical devices such as contact lenses, with an improved wettability may be obtained from novel amphiphilic block copolymers comprising a hydrophobic segment to which are covalently attached moieties comprising a crosslinkable ethylenically unsaturated group as well as surface-modifying hydrophilic segments.

- 20 The present invention therefore relates to an amphiphilic block copolymer of formula



wherein A is a hydrophobic polysiloxane or perfluoroalkyl polyether segment;

B is a surface-modifying hydrophilic segment having a weight average molecular weight of ≥ 100 that is devoid of a crosslinkable group;

- 25 Q is a moiety comprising at least one crosslinkable ethylenically unsaturated group;
(alk) is C₂-C₂₀-alkylene which is unsubstituted or substituted by hydroxy;

L_1 , L_2 and L_3 are each independently of the other a linking group;

p_1 and q_1 are each independently of the other an integer from 1 to 12; and either

t is 0 and p and q are each independently of the other an integer from 1 to 25; or

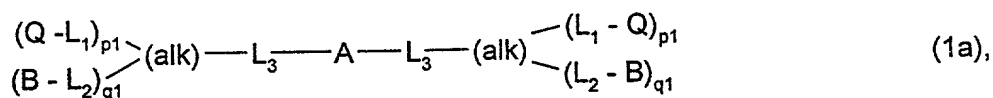
t is an integer from 1 to 8 and p and q are each 0.

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In case that t is 0, p and q are each independently of the other preferably an integer from 2 to 20, more preferably 2 to 15 and in particular 2 to 10. In case that p and q are each 0, t is preferably an integer from 1 to 6, more preferably 1 to 4 and in particular 2. p_1 is preferably an integer from 1 to 6, more preferably 1 to 4 and in particular 1 or 2. q_1 is preferably an integer from 1 to 10, more preferably 1 to 8, and in particular 1 to 4.

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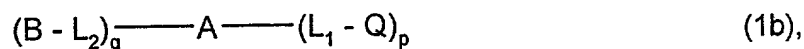
One group of suitable block copolymers of the invention conforms to the formula



wherein A , B , L_1 , L_2 , L_3 , Q , (alk), p_1 and q_1 are each as defined above.

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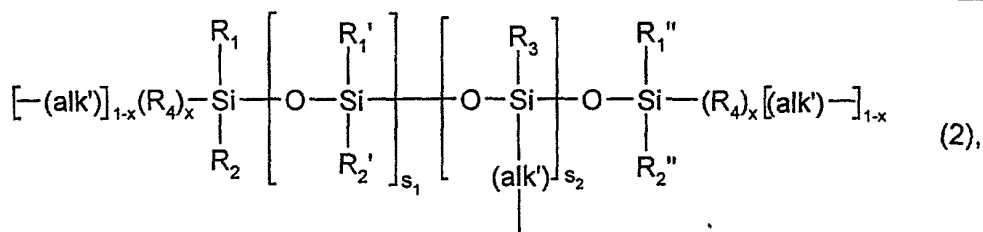
Another group of suitable block copolymers of the invention conforms to formula



wherein A , B , L_1 , L_2 and Q are each as defined above, and p and q are each independently of the other an integer from 1 to 25, preferably 2 to 20, more preferably 2 to 15 and in particular 2 to 10.

20

In one embodiment of the invention A is a polysiloxane segment of formula



wherein (alk') is alkylene having 1 to 20 carbon atoms which may be interrupted by -O-;

x is 0 or 1;

80 to 100 % of the radicals R_1 , R_1' , R_1'' , R_2 , R_2' , R_2'' , R_3 and R_4 , independently of one another, are C_1 - C_8 -alkyl, and 0-20% of the radicals R_1 , R_1' , R_1'' , R_2 , R_2' , R_2'' , R_3 and R_4 , independently of one another, are unsubstituted or C_1 - C_4 alkyl- or C_1 - C_4 -alkoxy-substituted phenyl, fluoro(C_1 - C_{18} -alkyl) or cyano(C_1 - C_{12} -alkyl),

s_1 is an integer from 5 to 700;

s_2 is the sum of (p+q+t-2) if x is 0, and is the sum of (p+q+t) if x is 1; wherein p, q and t are as defined above, and

the sum (s_1+s_2) is from 5 to 700.

In a preferred meaning of the polysiloxanes of formula (2), the sum (s_1+s_2) is an integer from 10 to 500, more preferably 10 to 300, even more preferably 20 to 150 and in particular preferably 50 to 140.

(alk') is preferably C_2 - C_8 -alkylene, which may be interrupted by -O- and more preferably C_2 - C_6 -alkylene which may be interrupted by -O-. Examples of particular preferred radicals (alk') are linear or branched C_2 - C_6 alkylene or a radical $-(CH_2)_{1-3}-O-(CH_2)_{1-3}-$, especially C_2 - C_4 -alkylene or a radical $-(CH_2)_{2-3}-O-(CH_2)_{2-3}-$.

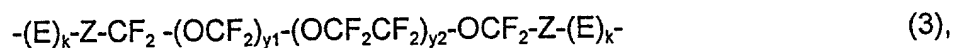
Preferably the radicals R_1 , R_1' , R_1'' , R_2 , R_2' , R_2'' , R_3 and R_4 are each independently of one another C_1 - C_6 -alkyl, more preferably each C_1 - C_4 -alkyl, more preferably each C_1 - C_2 -alkyl and in particular each methyl.

One embodiment of suitable polysiloxane hydrophobic blocks (A) encompasses a radical of the above formula (2), wherein x is 0, s₂ is 0, s₁ is an integer from 5 to 700, preferably 10 to 500, more preferably 10 to 300, even more preferably 20 to 150 and in particular preferably 50 to 140, R₁, R₁', R₁", R₂, R₂', R₂" and R₃ are each independently of one another C₁-C₈-alkyl, and for (alk') the above given meanings and preferences apply. In this case, either t in formula (1) is 0 and p and q are each 1, or, preferably, p and q are each 0 and t is 2.

Another embodiment of suitable polysiloxane hydrophobic blocks (A) encompasses a radical of the above formula (2), wherein x is 0, s₂ is the sum of (p+q+t-2), and for R₁, R₁', R₁", R₂, R₂', R₂", R₃, (alk'), p, q and t the above-given meanings and preferences each apply.

Still another embodiment of suitable polysiloxane hydrophobic blocks (A) encompasses a radical of the above formula (2), wherein x is 1, s₂ is the sum of (p+q+t), and for R₁, R₁', R₁", R₂, R₂', R₂", R₃, R₄, p, q and t the above-given meanings and preferences each apply.

In another embodiment of the invention, A is a perfluoroalkyl polyether segment of formula



in which y₁ + y₂ is a number in the range from 10 to 100; each Z, independently of the other, is a divalent radical having up to 12 carbon atoms or a bond; each E, independently of the others, is alkoxy, e.g. -(OCH₂CH₂)_r-, where r has a value of from 0 to 2 as a statistical average, and where the link -Z-E- represents the sequence -Z-(OCH₂CH₂)_r-; and k is 0 or 1;

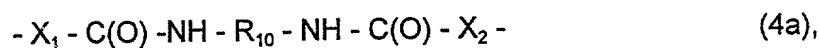
Z is preferably a bond, C₁-C₈-alkylene or -CONH-phenylene, in which the -CO- moiety is linked to a CF₂ group. Z is particularly preferably C₁-C₄-alkylene, in particular methylene.

The perfluoroalkoxy units OCF₂ and OCF₂CF₂ having the indices y₁ and y₂ in Formula (3) can have a random distribution. The sum of the indices y₁+y₂ is preferably a number in the range from 10 to 50, particularly preferably from 10 to 30. The ratio y₁:y₂ is preferably in the range from 0.5 to 1.5, in particular in the range from 0.8 to 1.2.

In one embodiment of the invention, the segment A may comprise one of the polymers illustrated above. According to another embodiment, the polymer in segment A may comprise more than one kind of polymers as illustrated above, e.g., may comprise polysiloxane subsegments of formula (2) and perfluoroalkylene polyether units of formula (3). Preferably, segment A is a polysiloxane of formula (2).

Segments A of the prepolymers of the invention have a mean molecular weight of for example in the range from about 1,000 to about 50,000, preferably in the range from about 1,500 to about 30000 and particularly preferably in the range from about 2,000 to about 20,000.

L_1 , L_2 and L_3 are each independently of the other, for example, a bivalent linking group of formula



wherein X_1 and X_2 are each independently of the other a group $-O-$, $-S-$ or $-NR_0-$, R_0 is hydrogen or C_1 - C_4 -alkyl, and R_{10} is linear or branched C_1 - C_{18} -alkylene or unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_6 - C_{10} -arylene, C_7 - C_{18} -aralkylene, C_6 - C_{10} -arylene- C_1 - C_2 -alkylene- C_6 - C_{10} -arylene, C_3 - C_8 -cycloalkylene, C_3 - C_8 -cycloalkylene- C_1 - C_6 -alkylene, C_3 - C_8 -cycloalkylene- C_1 - C_2 -alkylene- C_3 - C_8 -cycloalkylene or C_1 - C_6 -alkylene- C_3 - C_8 -cycloalkylene- C_1 - C_6 -alkylene.

The linking groups L_1 and L_2 of formulae (4a) - (4e) are to be understood that the left bond is in each case directed to A or (alk) and the right bond is directed to Q or B. The linking group L_3 of formulae (4a) - (4e) is to be understood that the left bond is directed to A and the right bond is directed to (alk).

If X_1 or X_2 is a group $-NR_0-$, R_0 is preferably methyl, ethyl or in particular hydrogen.

In formulae (4a)-(4e) X_1 and X_2 are each independently of the other preferably a group -O- or -NR₀- and more preferably -O- or -NH-.

5 R₁₀ as alkylene in formulae (4a) and (4b) is preferably linear or branched C₁-C₁₂-alkylene, more preferably C₁-C₆-alkylene and most preferably C₁-C₄-alkylene.

10 R₁₀ as alkylene in formula (4a) is preferably a linear or branched C₃-C₁₄alkylene radical, more preferably a linear or branched C₄-C₁₂alkylene radical and most preferably a linear or branched C₆-C₁₀alkylene radical. Some preferred alkylene radicals are 1,4-butylene, 2,2-dimethyl-1,4-butylene, 1,5-pentylene, 2,2-dimethyl-1,5-pentylene, 1,6-hexylene, 2,2,3- or 2,2,4-trimethyl-1,5-pentylene, 2,2-dimethyl-1,6-hexylene, 2,2,3- or 2,2,4- or 2,2,5-trimethyl-1,6-hexylene, 2,2-dimethyl-1,7-heptylene, 2,2,3- or 2,2,4- or 2,2,5- or 2,2,6-trimethyl-1,7-heptylene, 1,8-octylene, 2,2-dimethyl-1,8-octylene and 2,2,3- or 2,2,4- or 2,2,5- or 2,2,6- or 2,2,7-trimethyl-1,8-octylene.

15 20 When R₁₀ is arylene, it is, for example, naphthylene or especially phenylene, each of which may be substituted, for example, by C₁-C₄-alkyl or by C₁-C₄-alkoxy. Preferably, R₁₀ as arylene is 1,3- or 1,4-phenylene that is unsubstituted or substituted by C₁-C₄-alkyl or by C₁-C₄-alkoxy in the ortho-position to at least one linkage site. Examples of substituted arylene are 1-methyl-2,4-phenylene, 1,5-dimethyl-2,4-phenylene, 1-methoxy-2,4-phenylene and 1-methyl-2,7-naphthylene.

25 R₁₀ as aralkylene is preferably naphthylalkylene and most preferably phenylalkylene. The alkylene group in aralkylene contains preferably from 1 to 12, more preferably from 1 to 6 and most preferably from 1 to 4 carbon atoms. Most preferably, the alkylene group in aralkylene is methylene or ethylene. Some examples are 1,3- or 1,4-benzylene, naphth-2-yl-7-methylene, 6-methyl-1,3- or -1,4-benzylene and 6-methoxy-1,3- or -1,4-benzylene.

30 When R₁₀ is cycloalkylene, it is preferably C₅-C₆cycloalkylene and most preferably cyclohexylene that is unsubstituted or substituted by methyl. Some examples are 1,3-cyclobutylene, 1,3-cyclopentylene, 1,3- or 1,4-cyclohexylene, 1,3- or 1,4-cycloheptylene, 1,3- or 1,4- or 1,5-

cyclooctylene, 4-methyl-1,3-cyclopentylene, 4-methyl-1,3-cyclohexylene, 4,4-dimethyl-1,3-cyclohexylene, 3-methyl- or 3,3-dimethyl-1,4-cyclohexylene, 3,5-dimethyl-1,3-cyclohexylene and 2,4-dimethyl-1,4-cyclohexylene.

5 When R_{10} is cycloalkylene-alkylene, it is preferably cyclopentylene- C_1 - C_4 -alkylene and especially cyclohexylene- C_1 - C_4 -alkylene, each unsubstituted or mono- or poly-substituted by C_1 - C_4 -alkyl, especially methyl. More preferably, the group cycloalkylene-alkylene is cyclohexylene-ethylene and, most preferably, cyclohexylene-methylene, each unsubstituted or substituted in the cyclohexylene radical by from 1 to 3 methyl groups. Some examples are cyclopent-1-yl-3-methylene, 3-methyl-cyclopent-1-yl-3-methylene, 3,4-dimethyl-cyclopent-1-yl-3-methylene, 3,4,4-trimethyl-cyclopent-1-yl-3-methylene, cyclohex-1-yl-3- or -4-methylene, 3- or 4- or 5-methyl-cyclohex-1-yl-3- or -4-methylene, 3,4- or 3,5-dimethyl-cyclohex-1-yl-3- or -4-methylene and 3,4,5- or 3,4,4- or 3,5,5-trimethyl-cyclohex-1-yl-3- or -4-methylene.

15 When R_{10} is alkylene-cycloalkylene-alkylene, it is preferably C_1 - C_4 -alkylene-cyclopentylene- C_1 - C_4 -alkylene and especially C_1 - C_4 -alkylene-cyclohexylene- C_1 - C_4 -alkylene, each unsubstituted or mono- or poly-substituted by C_1 - C_4 -alkyl, especially methyl. More preferably, the group alkylene-cycloalkylene-alkylene is ethylene-cyclohexylene-ethylene and, most preferably, is methylene-cyclohexylene-methylene, each unsubstituted or substituted in the cyclohexylene radical by from 1 to 3 methyl groups. Some examples are cyclopentane-1,3-dimethylene, 3-methyl-cyclopentane-1,3-dimethylene, 3,4-dimethyl-cyclopentane-1,3-dimethylene, 3,4,4-trimethyl-cyclopentane-1,3-dimethylene, cyclohexane-1,3- or -1,4-dimethylene, 3- or 4- or 5-methyl-cyclohexane-1,3- or -1,4-dimethylene, 3,4- or 3,5-dimethyl-cyclohexane-1,3- or -1,4-dimethylene, 3,4,5- or 3,4,4- or 3,5,5-trimethyl-cyclohexane-1,3- or -1,4-dimethylene.

25 R_{10} as C_3 - C_8 -cycloalkylene- C_1 - C_2 -alkylene- C_3 - C_8 -cycloalkylene or C_6 - C_{10} -arylene- C_1 - C_2 -alkylene- C_6 - C_{10} -arylene is preferably C_5 - C_6 -cycloalkylene-methylene- C_5 - C_6 -cycloalkylene or phenylene-methylene-phenylene, each of which may be unsubstituted or substituted in the cycloalkyl or phenyl ring by one or more methyl groups.

The radical R_{10} in formula (4a) has a symmetrical or, preferably, an asymmetrical structure.

5 A preferred group of linking groups L_1 or L_2 comprises those of formula (4a), wherein R_{10} is linear or branched C_6 - C_{10} alkylene; cyclohexylene-methylene or cyclohexylene-methylene-cyclohexylene each unsubstituted or substituted in the cyclohexyl moiety by from 1 to 3 methyl groups; or phenylene or phenylene-methylene-phenylene each unsubstituted or substituted in the phenyl moiety by methyl.

10 The bivalent radical R_{10} in formula (4a) is derived preferably from a diisocyanate and most preferably from a diisocyanate selected from the group isophorone diisocyanate (IPDI), toluylene-2,4-diisocyanate (TDI), 4,4'-methylenebis(cyclohexyl isocyanate), 1,6-diisocyanato-2,2,4-trimethyl-n-hexane (TMDI), methylenebis(phenyl isocyanate), methylenebis(cyclohexyl-4-isocyanate) and hexamethylene diisocyanate (HMDI).

15 Another preferred group of linking groups L_1 or L_2 comprises those of formula (4b), wherein R_{10} is C_1 - C_6 -alkylene or 1,3- or 1,4-phenylene.

Further preferred linking groups L_1 or L_2 comprise $-O(O)C-$, $-C(O)O-$, $-HNC(O)-$, $-C(O)NH-$, $-OC(O)O-$ and $HNC(O)NH-$.

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A preferred group of linking groups L_3 comprises those of formula (4b) or (4c), wherein the above meanings and preferences apply.

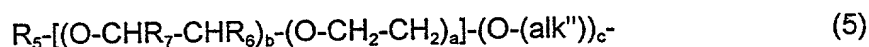
Suitable hydrophilic segments B are for example:

- 25 (i) non-ionic segments, for example a polyoxyalkylene, polysaccharid, polypeptide, poly(vinylpyrrolidone), polyhydroxyalkylacrylate or -methacrylate, polyacyl alkylene imine, polyacryl amide, polyvinyl alcohol, polyvinyl ether or polyol;
- (ii) polyionic segments, for example a polycationic segment such as a polyallylammonium, polyethyleneimine, polyvinylbenzyltrimethylammonium, polyaniline, sulfonated polyaniline,
- 30 polypyrrole or polypyridinium segment, or a polyanionic segment such as a polyacrylic or

polymethacrylic acid, a polythiophene-acetic acid, a polystyrenesulfonic acid, or a zwitterionic segment. Polyionic segments in each case encompass the free amine, imine or acid or a suitable salt thereof.

- 5 Some examples of preferred hydrophilic segments B are a polyoxyalkylene, such as a polyethylene glycol or polypropylene glycol or a block copolymer thereof, a poly(vinylpyrrolidone), poly(hydroxyethylacrylate), poly(hydroxyethylmethacrylate), polyacrylamide, poly(N,N-dimethylacrylamide), polyacrylic or polymethacrylic acid, a polyacyl alkylene imine or a copolymeric mixture of two or more of the above-mentioned polymers.

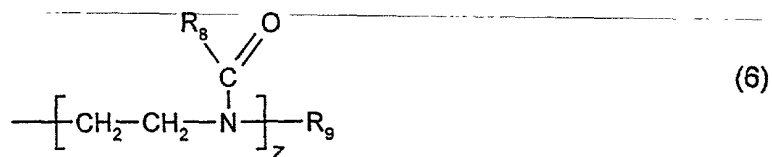
10 B as a polyoxyalkylene radical may correspond, for example, to formula



- 15 wherein R_5 is hydrogen, C_1 - C_{24} -alkyl, C_1 - C_{24} -alkanoyl or a radical $-(alk'')-NH_2$, one of the radicals R_6 and R_7 is hydrogen and the other is methyl, (alk'') is C_1 - C_6 -alkylene, c is the number 0 or 1, and each of a and b independently of the other is a number from 0 to 100, the sum of $(a+b)$ being from 2 to 100.

- 20 In formula (5), R_5 is preferably hydrogen, C_1 - C_4 -alkyl or C_1 - C_4 -alkanoyl, more preferably hydrogen or C_1 - C_2 -alkyl and in particular hydrogen. (alk'') is preferably C_2 - C_4 -alkylene and in particular 1,2-ethylene or 1,2- or 1,3-propylene. The variable c preferably is an integer of 0. Each of a and b independently of the others is preferably a number from 0 to 80, the sum of $(a+b)$ being from 3 to 80. Most preferably, each of a and b independently of the others is a
- 25 number from 0 to 50, the sum of $(a+b)$ being from 4 to 50 and especially from 8 to 50. A preferred embodiment relates to polyoxyalkylene segments of formula (5) wherein b and c are each 0, R_5 is hydrogen, C_1 - C_4 -alkyl or C_1 - C_4 -alkanoyl, and for the variable a the above-mentioned meanings and preferences apply.

- 30 B as a polyacyl alkylene imine may correspond, for example, to a segment of formula



wherein R₈ is hydrogen; C₁-C₁₂-alkyl unsubstituted or substituted by hydroxy or fluoro and/or uninterrupted or interrupted by oxygen; C₅-C₈-cycloalkyl; phenyl; or benzyl, R₉ is, for example, C₁-C₁₂-alkyl, benzyl, C₂-C₄-alkanoyl, benzoyl or phenyl, preferably C₁-C₆-alkyl, acetyl or benzyl and in particular C₁-C₄-alkyl, and z is an integer from 2 to 150.

R₈ is preferably C₁-C₈-alkyl which is unsubstituted or substituted by hydroxy or fluorine and/or is uninterrupted or interrupted by -O-; or is C₃-C₈-alkenyl. R₈ is more preferably C₁-C₄-alkyl, hydroxy-C₁-C₄-alkyl or trifluoromethyl and most preferably methyl. z is preferably an integer from 4 to 100, more preferably 4 to 50 and especially 5 to 20.

The mean weight average molecular weight of the hydrophilic blocks B may vary within wide limits. A preferred embodiment of the invention relates to prepolymers, particularly to prepolymers for ophthalmic uses, wherein segments B have a mean molecular weight in the range from about 200 to about 10,000, preferably in the range from about 350 to about 5000 and particularly preferably in the range from about 500 to about 1,500.

The hydrophilic blocks B are preferably linked to A or (alk) by a linking group L₂ of formula (4a).

Q is, for example, a crosslinkable or polymerizable group Q₁ or a hydrophilic segment comprising a crosslinkable or polymerizable group such as Q₁.

Q as a group Q₁ is, for example, a radical of formula



wherein (Alk) is linear or branched C₁-C₁₂-alkylene, X is -O- or -NH-, R₁₁ is an olefinically unsaturated copolymerisable radical having from 2 to 24 carbon atoms which may be further substituted, and w is the number 0 or 1.

- 5 Suitable substituents on the olefinic C₂-C₂₄ radical R₁₁ are, for example, C₁-C₄alkoxy, halogen, phenyl or carboxy. R₁₁ is, for example, a radical of formula



wherein l is the number 0 or 1, R₁₂ is hydrogen, C₁-C₄-alkyl or halogen, each of R₁₃ and R₁₄ independently of the other is hydrogen, C₁-C₄-alkyl, phenyl, carboxy or halogen, and R₁₅ is linear or branched C₁-C₁₂-alkylene or unsubstituted or C₁-C₄-alkyl- or C₁-C₄-alkoxy-substituted phenylene or C₇-C₁₂-aralkylene.

When R₁₅ is a phenylene radical, it is, for example, unsubstituted or methyl- or methoxy-substituted 1,2-, 1,3- or 1,4-phenylene. Preferably, R₁₅ as a phenylene radical is 1,3- or 1,4-phenylene.

When R₁₅ is an aralkylene radical, it is, for example, unsubstituted or methyl- or methoxy-substituted benzylene, wherein the methylene group is bonded to the amine nitrogen in each case. Preferably, Z' as an aralkylene radical is the 1,3- or 1,4-phenylenemethylene radical, wherein the methylene group is bonded to the amine nitrogen -NH- in each case.

R₁₅ is preferably unsubstituted or methyl- or methoxy-substituted phenylene or phenylene-methylene or C₁-C₁₂alkylene, more preferably 1,3- or 1,4-phenylene or C₁-C₆alkylene, especially C₁-C₂alkylene and most preferably methylene.

l is the number 1 or, preferably, the number 0. R₁₂ is preferably hydrogen, methyl or chlorine and most preferably hydrogen or methyl.

Each of R_{13} and R_{14} independently of the other is preferably hydrogen, carboxy, chlorine, methyl or phenyl. In a preferred embodiment of the invention, R_{13} is hydrogen, chlorine, methyl or phenyl and R_{14} is hydrogen or carboxy. Most preferably, R_{13} and R_{14} are each hydrogen.

- 5 Examples of suitable radicals R_{11} are vinyl, 1-methylvinyl, 2-propenyl, allyl, 2-butenyl, o-, m- or p-vinylphenyl, styryl, 2-carboxyvinyl, 2-chloro-2-carboxyvinyl, 1,2-dichloro-2-carboxyvinyl, 1,2-dimethyl-2-carboxyvinyl and 2-methyl-2-carboxyvinyl.

Especially preferred radicals R_{11} correspond to formula (8) wherein l is 0, R_{12} is hydrogen or methyl, R_{13} is hydrogen, methyl, chlorine or phenyl, in particular hydrogen, and R_{14} is carboxy or particularly hydrogen.

Other especially preferred radicals R_{11} correspond to the above formula (8) wherein l is 1, R_{15} is 1,3- or 1,4-phenylene or C_1 - C_6 -alkylene, especially C_1 - C_2 -alkylene, R_{12} is hydrogen or methyl and R_{13} and R_{14} are each hydrogen.

(Alk) is preferably C_1 - C_4 -alkylene, especially methylene or 1,1-dimethylmethylene.

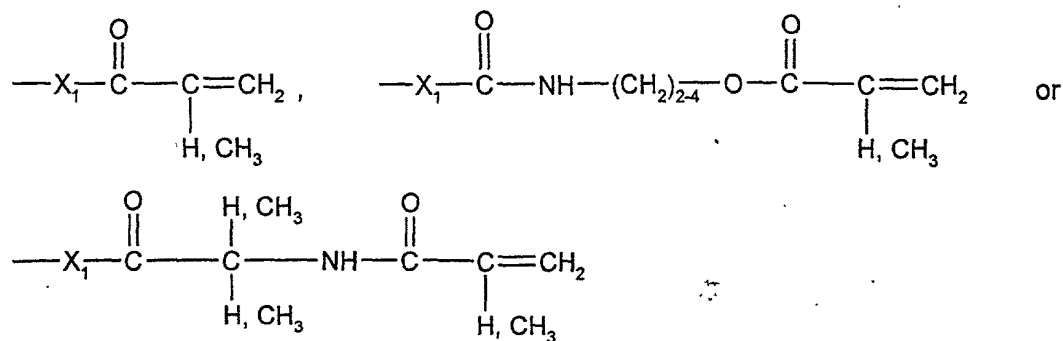
The crosslinkable or polymerizable group Q_1 is preferably linked to A or (alk) by a linking group L_1 of formula (4a), (4c) or (4e).

One group of suitable radicals L_1 - Q_1 are those wherein L_1 is a radical of formula (4c) wherein X_1 is -NH- or in particular -O-, Q_1 corresponds to a radical of the above formula (7) wherein w is 0, and for R_{11} the above given meanings and preferences apply.

- 25 A second group of suitable radicals L_1 - Q_1 are those wherein L_1 is a radical of formula (4c) wherein X_1 is -NH- or in particular -O-, Q_1 corresponds to a radical of the above formula (7) wherein w is 1, and for R_{11} the above given meanings and preferences apply.

- Still another group of suitable radicals L_1 - Q_1 are those wherein L_1 is a radical of formula (4e) wherein X_1 is -NH- or in particular -O-, X_2 is -NH-, Q_1 corresponds to a radical of the above
30 formula (7) wherein w is 1, and for R_{11} the above given meanings and preferences apply.

Especially preferred radicals -L₁-Q₁ correspond to formula

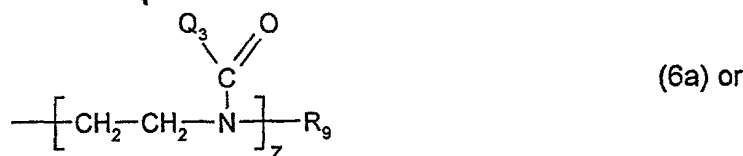
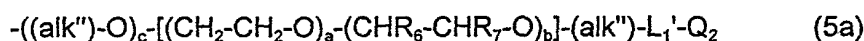


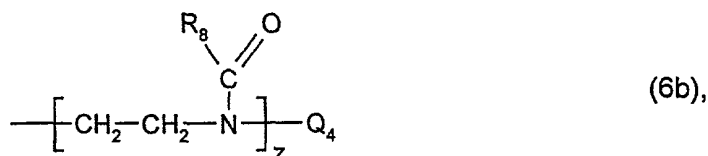
wherein X₁ is -O- or -NH-, in particular -O-.

Q as a hydrophilic segment comprising a crosslinkable or polymerizable C-C double bond group is, for example a polyoxyalkylene, such as a polyethylene glycol or polypropylene glycol or a block copolymer thereof, a poly(vinylpyrrolidone), poly(hydroxyethylacrylate), poly(hydroxyethylmethacrylate), polyacrylamide, poly(N,N-dimethylacrylamide), polyacrylic or polymethacrylic acid, a polyacyl alkylene imine or a copolymeric mixture of two or more of the above-mentioned polymers which in each case comprises one or more, preferably 1, ethylenically unsaturated bond and has a weight average molecular weight of, for example, ≥ 100 .

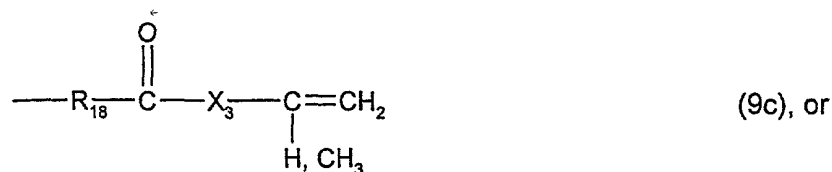
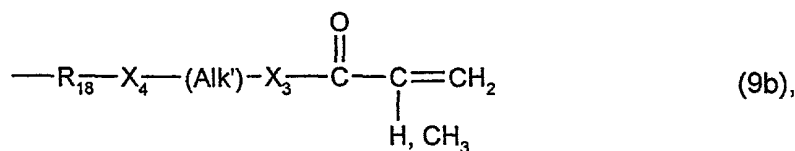
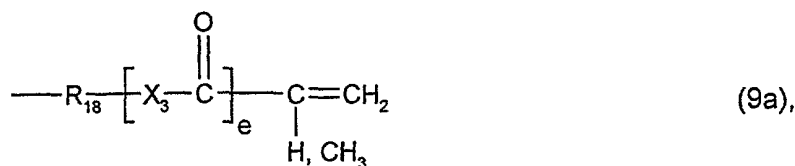
C-C double bond containing hydrophilic segments Q advantageously have a mean molecular weight in the range from about 200 to about 10,000, preferably in the range from about 350 to about 5000 and particularly preferably in the range from about 500 to about 1,500.

Examples of suitable C-C double bond containing hydrophilic segments Q are a radical of formula





wherein for L_1' and Q_2 each the meanings and preferences given above for L_1 and Q_1 apply, Q_3 is C_3 - C_{12} -alkenyl or a radical $-(CH_2)_{1-4}-O-R_{16}$ wherein R_{16} is acryloyl, methacryloyl or a group $-C(O)-NH-(CH_2)_{2-4}-O-C(O)-C(R_{17})=CH_2$ and R_{17} is hydrogen or methyl, Q_4 is a radical of formula



wherein X_3 is $-O-$ or $-NR$, R is hydrogen or C_1 - C_4 -alkyl, X_4 is a group $-C(O)-O-$, $-O-C(O)-NH-$ or $-NH-C(O)-O-$, (Alk') is C_1 - C_8 -alkylene, e is an integer of 0 or 1, and R_{18} is C_1 - C_{12} -alkylene, phenylene or C_7 - C_{12} -phenylenealkylene, and for R_6 , R_7 , R_8 , R_9 , (alk'') , a , b , c and z each the above-given meanings and preferences apply.

Q_3 in formula (6a) is preferably a radical $-(CH_2)_{2-4}-O-R_{16}$ wherein R_{16} is acryloyl, methacryloyl or a group $-C(O)-NH-(CH_2)_2-O-C(O)-C(R_{17})=CH_2$, and R_{17} is hydrogen or methyl.

Preferred meanings of the variables contained in formulae (9a)-(9d) are:

R is preferably methyl, ethyl or, in particular, hydrogen. X_3 in formula (9a) is preferably -O- or -NH-. X_3 in formula (9b) is preferably -NH-. X_3 in formula (9c) is preferably -O-. X_4 is preferably the radical -NH-C(O)-O-. R_{18} is preferably C_1 - C_6 -alkylene, or benzyl and more preferably C_1 - C_4 -alkylene or benzyl, and most preferably methyl, ethyl or benzyl. (Alk') is preferably C_2 - C_6 -alkylene and in particular C_2 - C_4 -alkylene. e is preferably the number 1.

Some examples of suitable radicals Q_4 are o-, m- or p-vinylbenzyl, allyl, acryloyl- C_1 - C_4 -alkyl, in particular acryloylethyl, methacryloyl- C_1 - C_4 -alkyl, in particular methacryloylethyl, acrylamido- C_1 - C_4 -alkyl, in particular acrylamidoethyl, methacrylamido- C_1 - C_4 -alkyl, in particular methacrylamidoethyl, vinyloxycarbonyl- C_1 - C_4 -alkyl, in particular vinyloxycarbonylmethyl or vinyloxycarbonylethyl, and vinylcarbonyl.

Q as a hydrophilic block comprising an ethylenically unsaturated group is preferably linked to A or (alk) by a linking group L_1 of formula (4a).

(alk) is preferably C_2 - C_{12} -alkylene, more preferably C_3 - C_{10} -alkylene and most preferably C_4 - C_8 -alkylene, which is in each case unsubstituted or substituted by hydroxy. (alk) is preferably linked to A by a linking group L_3 of formula (4a) or (4c).

The amphiphilic block copolymers of the invention wherein t is 0 and L_1 and L_2 are each a linking group of formula (4a) or (4b) may be prepared, for example, by reacting in any order a compound of formula



about (p+q) molar equivalents of a compound of formula



about p molar equivalents of a compound of formula



and about q molar equivalents of a compound of formula



each, wherein Y is a group $-\text{N}=\text{C}=\text{O}$ or carboxy or a suitable derivative thereof, for example a group $-\text{C}(\text{O})\text{OH}$, $-\text{C}(\text{O})\text{OR}_{19}$ or $-\text{C}(\text{O})-\text{OHal}$ wherein R_{19} is, for example, C_1 - C_4 -alkyl, phenyl or benzyl and Hal is halogen, in particular bromine or chlorine, X_2' independently has the meaning of X_2 , and A, B, X_1 , X_2 , p and q are as defined above.

For example, the compounds of formulae (12) and (13) may be first reacted with about one molar equivalent of a compound of formula (11) each, and the intermediates obtained are then reacted with the compound of formula (10). Another synthetic route comprises first reacting a compound of formula (10) with a compound of formula (11), and the intermediate obtained is then reacted with a mixture of the compounds of formulae (12) and (13).

Where the compound of formula (11) is a carboxylic acid or a derivative thereof, e.g. a carboxylic acid halide, the reaction thereof with the components of formulae (10), (12) and (13), respectively, can be carried out under the conditions that are customary for ester, thioester, or amide formation, for example at temperatures of, for example, from -40 to 80°C , preferably from 0 to 50°C and most preferably from 0 to 25°C , in a dipolar aprotic solvent, e.g. tetrahydrofuran, dioxane, DMSO or an aprotic solvent as mentioned below, or in a mixture of water and one of the mentioned solvents, in the presence of a base, e.g. an alkali metal hydroxide, and, where applicable, in the presence of a stabiliser. Suitable stabilisers are, for example, 2,6-dialkylphenols, hydroquinone derivatives, e.g. hydroquinone or hydroquinone monoalkyl ethers, or N-oxides, e.g. 4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-yl. The reaction times may vary within wide limits, a period of, for example, from 30 minutes to 12 hours, preferably from 1 to 6 hours and especially from 2 to 3 hours, generally having been found practicable.

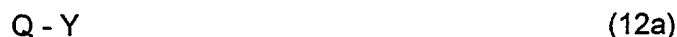
Where the compound of formula (11) is an isocyanate, the reaction thereof with the components of formulae (10), (12) and (13), respectively, can be carried out under the conditions that are customary for the formation of urethanes or ureas. In case of urethane formation it is advantageously to perform the reaction in an inert solvent. Amines of the formula (10), (12) and (13) may be reacted with the diisocyanate of formula (11) also in an aqueous medium. It is

especially advantageous to use diisocyanates having isocyanate groups of differing reactivity since the formation of isomers and diadducts can thereby be substantially suppressed. The differing reactivity can be brought about, for example, by steric hindrance.

- 5 Suitable inert solvents for the reaction of the compounds of formulae (10), (12) or (13) with a compound of formula (11) are aprotic, preferably polar, solvents, for example hydrocarbons (petroleum ether, methylcyclohexane, benzene, toluene, xylene), halogenated hydrocarbons (chloroform, methylene chloride, trichloroethane, tetrachloroethane, chlorobenzene), ethers (diethyl ether, dibutyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran, dioxane), ketones (acetone, dibutyl ketone, methyl ethyl ketone, methyl isobutyl ketone), carboxylic acid esters and lactones (ethyl acetate, butyrolactone, valerolactone), alkylated carboxylic acid amides (N,N-dimethylacetamide, N-methylpyrrolidone), nitriles (acetonitrile), sulfones and sulfoxides (dimethyl sulfoxide, tetramethylenesulfone). Polar solvents are preferably used. The reaction temperature may be, for example, from -40 to 200°C.
- 15 When catalysts are used, the temperatures may advantageously be in the range of from 0 to 50°C, preferably at room temperature. Suitable catalysts are, for example, metal salts, such as ferric chloride or alkali metal salts of carboxylic acids, tertiary amines, for example (C₁-C₆alkyl)₃N (triethylamine, tri-n-butylamine), N-methylpyrrolidine, N-methylmorpholine, N,N-dimethylpiperidine, pyridine and 1,4-diaza-bicyclooctane. Tin salts have been found to be especially effective, especially alkyltin salts of carboxylic acids, for example dibutyltin dilaurate and tin dioctoate. The isolation and purification of the compounds prepared is carried out according to known methods, for example by means of extraction, crystallisation, recrystallisation or chromatographic purification methods.
- 25 The amphiphilic block copolymers of the invention wherein t is 0 and L₁ and L₂ are each a linking group of formulae (4c), (4d) or (4e) may be prepared, for example, by reacting a compound of the formula



with about p molar equivalents of a compound of the above formula (12) and q molar equivalents of a compound of formula (13), or by reacting a compound of the above formula (10) with about p molar equivalents of a compound of formula



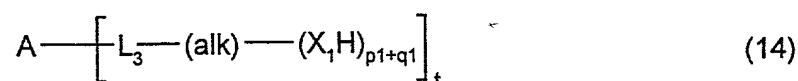
5 and about q molar equivalents of a compound of formula



wherein A, B, Q, Y, p and q each have the above-mentioned meaning.

The reaction of the components of formulae (10a) and (12) and (13) or (10) and (12a) and (13a), respectively, can be carried out under the conditions that are customary for ester, thioester, amide, urethane or urea formation, for example as outlined above.

The amphiphilic block copolymers of the invention wherein p and q are each 0 and L_1 and L_2 are each a linking group of formula (4a), (4b), (4c) or (4e) may be prepared, for example, by reacting a compound of formula



with

(i) about p1 molar equivalents of a compound of formula (12a) or the reaction product of a compound of formula (11) and (12); and

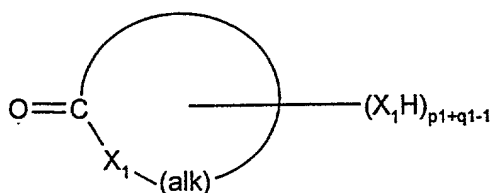
20 (ii) about q1 molar equivalents of a compound of formula (13a) or the reaction product of a compound of formula (11) and (13),

wherein A, L_3 , X_1 , (alk), p1 and q1 are each as defined above.

The reactions can be carried out under the conditions that are customary for ester, thioester, amide, urethane or urea formation, for example as outlined above. A linking group L_1 or L_2 of formula (4d) in the above amphiphilic block copolymers may be prepared, for example, by reacting a compound which is analogous to the compound of formula (14) but contains a

carboxy group or an above-mentioned derivative thereof with a compound of formula (12) or (13).

The compounds of formula (14) are known or may be prepared according to processes known in the art, for example by reacting a compound $A-(X_1H)_t$ with a compound $Y_1-(alk)-(X_1'H)_{p1+q1}$ or



wherein X_1' independently has the meaning of X_1 , Y_1 is carboxy or an above-mentioned derivative thereof, and X_1 , (alk), $p1$ and $q1$ each have the above-mentioned meaning.

The molecular weight of the copolymers of the invention is, within wide limits, not critical. Preferably, however, the prepolymer has a weight average molecular weight of from approximately 1400 to 200000, preferably from 2000 to 100000 and more preferably from 2500 to 50000 and most preferably from 3000 to 25000.

The amphiphilic block copolymers of formula (1) are crosslinkable, but are uncrosslinked or, at least, substantially uncrosslinked; in addition, they are stable, that is to say spontaneous crosslinking as a result of homopolymerisation does not take place.

The amphiphilic block copolymers of formula (1) according to the invention are crosslinkable in a controlled and extremely effective manner, especially by photo-crosslinking.

The present invention further relates, therefore, to a polymer that can be obtained by photo-crosslinking of a amphiphilic block copolymers of formula (1), in the presence or, preferably, in the absence of an additional vinyl comonomer. These crosslinked polymers are water-insoluble.

In the photo-crosslinking, a photoinitiator capable of initiating free-radical crosslinking is suitably

added. Examples thereof will be familiar to the person skilled in the art, suitable photoinitiators that may specifically be mentioned being benzoin methyl ether, 1-hydroxycyclohexylphenyl ketone, Darocure 1173 or Irgacure types. The crosslinking can then be brought about by actinic radiation, e.g. UV light, or ionising radiation, e.g. gamma rays or X-rays. The amount of photoinitiator may be selected within wide limits, an amount of up to 0.05 g/g of polymer and especially of up to 0.01 g/g of polymer having proved beneficial.

The amphiphilic block copolymers of formula (1) is introduced into the crosslinking process preferably in pure form, particularly substantially free from undesired constituents, such as, for example, free from monomeric, oligomeric or polymeric starting compounds used for the preparation of the copolymer, and/or free from secondary products formed during the preparation of the copolymer. Said copolymers in pure form are obtained advantageously by previously purifying them in a manner known per se, for example by precipitation with a suitable solvent, filtration and washing, extraction in a suitable solvent, dialysis, reverse osmoses (RO) or ultrafiltration, reverse osmoses and ultrafiltration being especially preferred.

The preferred purification processes for the copolymers of the invention, reverse osmoses and ultrafiltration, can be carried out in a manner known per se. It is possible for the ultrafiltration and reverse osmoses to be carried out repeatedly, for example from two to ten times. Alternatively, the ultrafiltration and reverse osmoses can be carried out continuously until the selected degree of purity is attained. The selected degree of purity can in principle be as high as desired.

The copolymers of formula (1) may be crosslinked, for example, in form of a solution or a mesophase.

One embodiment of the invention relates to the photo-polymerisation of the block copolymers of the invention in solution, preferably in one or more different organic solvents. Suitable solvents are in principle all solvents that dissolve the polymers according to the invention and an optional vinyl comonomer which may be additionally used, e.g. alcohols, such as C₁-C₆-alkanols, e.g. n- or iso-propanol, ethanol or methanol, carboxylic acid amides, such as dimethylformamide, or

dimethyl sulfoxide, and mixtures of suitable solvents, e.g. mixtures of water with an alcohol, e.g. a water/propanol, water/ethanol or a water/methanol mixture.

According to this embodiment of the invention, the photo-crosslinking is preferably effected from a solution comprising (i) one or more prepolymers according to the invention which can be obtained as a result of the preferred purification step, ultrafiltration, (ii) one or more solvents selected from the group consisting of a C₁-C₆- alkanol, a carboxylic acid amide, dimethyl sulfoxide and water, and optionally (iii) an additional vinyl comonomer. For example, photo-crosslinking of the block copolymers is carried out in ethanol or n- or iso-propanol.

The vinyl comonomer that can additionally be used according to the invention in the photo-crosslinking may be hydrophilic or hydrophobic or may be a mixture of a hydrophobic and a hydrophilic vinyl monomer. Suitable vinyl monomers include especially those which are customarily used in the manufacture of contact lenses. The expression "hydrophilic vinyl monomer" is understood to mean a monomer that typically produces as homopolymer a polymer that is water-soluble or capable of absorbing at least 10 % by weight water. Analogously, the expression "hydrophobic vinyl monomer" is understood to mean a monomer that typically produces as homopolymer a polymer that is water-insoluble or capable of absorbing less than 10 % by weight water.

The proportion of vinyl comonomers, if used, is preferably from 0.5 to 80 units per copolymer of formula (1), especially from 1 to 30 units of vinyl comonomer per copolymer unit of formula (1) and most preferably from 5 to 20 units per copolymer of formula (1).

It is also preferred to use a hydrophobic vinyl comonomer or a mixture of a hydrophobic vinyl comonomer with a hydrophilic vinyl comonomer, the mixture containing at least 50 % by weight of a hydrophobic vinyl comonomer. In that manner, the mechanical properties of the polymer can be improved without the water content being appreciably reduced. In principle, however, both conventional hydrophobic vinyl comonomers and conventional hydrophilic vinyl comonomers are suitable for copolymerisation with a prepolymer of formula (1).

Suitable hydrophobic vinyl comonomers include, without the following being an exhaustive list, C₁-C₁₈alkyl acrylates and methacrylates, C₃-C₁₈alkylacrylamides and -methacrylamides, acrylonitrile, methacrylonitrile, vinyl-C₁-C₁₈alkanoates, C₂-C₁₈alkenes, C₂-C₁₈haloalkenes, styrene, C₁-C₆alkylstyrene, vinyl alkyl ethers in which the alkyl moiety has from 1 to 6 carbon atoms, C₂-C₁₀perfluoroalkyl acrylates and methacrylates or correspondingly partially fluorinated acrylates and methacrylates, C₃-C₁₂perfluoroalkyl-ethyl-thiocarbonylaminoethyl acrylates and methacrylates, acyloxy- and methacyloxy-alkylsiloxanes, N-vinylcarbazole, C₁-C₁₂alkyl esters of maleic acid, fumaric acid, itaconic acid, mesaconic acid and the like. Preferred are, for example, C₁-C₄alkyl esters of vinylically unsaturated carboxylic acids having from 3 to 5 carbon atoms or vinyl esters of carboxylic acids having up to 5 carbon atoms.

Examples of suitable hydrophobic vinyl comonomers include methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, styrene, chloroprene, vinyl chloride, vinylidene chloride, acrylonitrile, 1-butene, butadiene, methacrylonitrile, vinyltoluene, vinyl ethyl ether, perfluorohexylethylthiocarbonylaminoethyl methacrylate, isobornyl methacrylate, trifluoroethyl methacrylate, hexafluoroisopropyl methacrylate, hexafluorobutyl methacrylate, tris-trimethylsilyloxy-silyl-propyl methacrylate, 3-methacyloxypropylpentamethyldisiloxane and bis(methacyloxypropyl)-tetramethyldisiloxane.

Suitable hydrophilic vinyl comonomers include, without the following being an exhaustive list, hydroxy-substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, lower alkylacrylamide and -methacrylamide, ethoxylated acrylates and methacrylates, hydroxy-substituted lower alkylacrylamides and methacrylamides, hydroxy-substituted lower alkyl vinyl ethers, sodium ethylenesulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinylsuccinimide, N-vinylpyrrolidone, 2- or 4-vinylpyridine, acrylic acid, methacrylic acid, amino- (the term "amino" also including quaternary ammonium), mono-lower alkylamino- or di-lower alkylamino-lower alkyl acrylates and

methacrylates, allyl alcohol and the like. Preferred are, for example, hydroxy-substituted C₂-C₄alkyl (meth)acrylates, five- to seven-membered N-vinyl lactams, N,N-di-C₁-C₄alkyl(meth)-acrylamides and vinylically unsaturated carboxylic acids having a total of from 3 to 5 carbon atoms.

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Examples of suitable hydrophilic vinyl comonomers include hydroxyethyl methacrylate, hydroxyethyl acrylate, acrylamide, methacrylamide, dimethylacrylamide, allyl alcohol, vinylpyridine, vinylpyrrolidine, glycerol methacrylate, N-(1,1-dimethyl-3-oxobutyl)-acrylamide and the like.

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Preferred hydrophobic vinyl comonomers are methyl methacrylate and vinyl acetate. Preferred hydrophilic vinyl comonomers are 2-hydroxyethyl methacrylate, N-vinylpyrrolidone and acrylamide. Most preferably, the crosslinking of the copolymers of formula (1) is carried out in the absence of a vinylic comonomer.

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According to another preferred embodiment of the invention, the copolymers of formula (1) are previously converted into a mesophase which is at least partly bicontinuous, and the mesophase is then subjected to photocrosslinking. A suitable process producing a mesophase composition is disclosed in PCT patent application WO 99/12059, which application is herein incorporated by reference.

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The term mesophase in this context is to be understood as meaning a thermodynamically stable mixture of an amphiphilic substance such as a crosslinkable block copolymer of formula (1) and an aqueous solution or a melt of an above-mentioned crosslinkable amphiphilic block copolymer which shows in each case a self-assembled microstructure. Mesophases are typically homogeneous and optical transparent mixtures which lie in single phase regions of the phase diagram of the components the system is based on. These single phases may be of a liquid crystalline nature (such as lamellar, hexagonal or cubic) which indicates an ordered compartmentisation of components in the mixture with a geometrically regular and repeated structure, or may be of a non-crystalline nature in which compartmentisation is random and

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isotropic. An example for this latter type of mesophases is represented by microemulsions. Accordingly, many microstructures can occur within the general class of mesophases. Within the present invention, mesophases having a liquid crystalline microstructure are preferred. The mesophases of the claimed process thus preferably lie in single phase regions of the phase diagram that exhibit a crystalline structure and most preferably a cubic structure.

In addition, the mesophases of this embodiment are at least partly bicontinuous, that is to say the mixture has at least two partly bicontinuous phases, for example an oxygen-permeable and an ion-permeable phase, which are intermingled.

A "phase", as used herein, refers to a region of substantially uniform composition which is a distinct and physically separate portion of a heterogeneous polymeric material. However, the term "phase" does not imply that the material described is a chemically pure substance, but merely that certain bulk properties differ significantly from the properties of another phase within the material. Thus, with respect to the polymeric components of an ophthalmic molding such as a lens, an ion-permeable phase refers to a region composed of essentially only ion-permeable polymer (and water, when hydrated), while an oxygen-permeable phase refers to a region composed of essentially only oxygen-permeable polymer (and perhaps a small amount of water, when hydrated).

"Bicontinuous phases", as used herein, refers to at least two regions, each of substantially uniform composition which differs from the other, and each of which exhibiting its individual properties. With respect to ophthalmic moldings such as contact lenses it has been found that it is highly desirable to have bicontinuous phases of an oxygen-permeable polymer and an ion-permeable polymer which provide the lens with two continuous pathways or sets of continuous pathways extending from the inner surface of the lens to the outer surface of the lens. Said at least two continuous pathways ensure that the lens material has both a high oxygen transmissibility and ion or water permeability.

The mesophases may be prepared from a melt of one or more than one different copolymers of formula (1) and optionally further components or, preferably, from (i) one or more than one different copolymers of formula (1), (ii) an aqueous solution and optionally (iii) further components.

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(ii) aqueous solution;

The aqueous solution that is added to form the mesophase may be pure water or a mixture of water and one or more water-miscible solvents and/or salts.

(ii-a) water-miscible organic solvents;

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Examples of suitable solvents that may be added to the mesophase are a monohydric or polyhydric alcohol, for example a C₁-C₈ alcohol such as n-butanol, n-propanol, ethanol or methanol or a polyhydric alcohol such as glycerol or a glycol; a polyether such as Butyl Cellosolve™, Butyl Carbitol™, Hexyl Cellosolve™, or Hexyl Carbitol™; a carboxylic acid amide, for example N,N-dimethylformamide; acetone, acetonitrile; dimethyl sulfoxide; or mixtures thereof. Preferably, the aqueous solution does not comprise any additional organic solvent or comprises a C₁-C₄ alcohol, for example ethanol or methanol as additional organic solvent. In a particularly preferred embodiment of the invention, the aqueous solution does not comprise an additional organic solvent.

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(ii-b) salts;

Salts that may be comprised in the aqueous solution used to form the inventive mesophases include without limitation thereto physiologically tolerable salts, such as buffer salts customary in the field of contact lens care, for example phosphate salts, or isotonicising agents customary in the field of contact lens care, such as alkali halides, for example sodium chloride, or mixtures thereof.

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If salts are added, the aqueous salt solution has for example an osmolarity of from about 200 to 450 milliosmol in 1000 ml (unit: mOsm/l), preferably an osmolarity of from about 250 to 350 mOsm/l, and in particular about 300 mOsm/l.

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An example of an especially suitable aqueous salt solution of the invention is an artificial, preferably buffered, lacrimal fluid that in respect of pH value and osmolarity is adapted to natural lacrimal fluid, for example, a sodium chloride solution that is unbuffered or that is preferably buffered, for example, by a phosphate buffer, and that has an osmolarity that corresponds to the osmolarity of human lacrimal fluid.

The aqueous solution employed for the formation of the mesophases of the invention is preferably a pure solution which means a solution which is free or essentially free from undesired constituents. Especially preferred examples of such solutions are pure water or an artificial lacrimal fluid, as defined hereinbefore.

(iii) optional further components;

Optional further components which are used for the preparation of the mesophases, besides the crosslinkable block copolymer of formula (1) and the aqueous solution, are for example: (iii-a) a photoinitiator, for example one of the photoinitiators mentioned above; (iii-b) a surfactant which may be any conventional non-ionic, cationic or zwitterionic surfactant known in the art; (iii-c) a hydrophobic or hydrophilic comonomer wherein the above given meanings and preferences apply; or (iii-d) a pharmaceutical effective agent, for example a protein, enzyme, vitamin, disinfectant, bactericide or the like.

The mesophases of the present invention may be prepared by simply admixing suitable amounts of the copolymer of formula (1), the aqueous solution and optionally further components in any order at a temperature of, for example, 0 to 100°C, preferably 10 to 50°C, and more preferably 15 to 40°C. The mesophases may form spontaneously or upon stirring and/or standing for a suitable period. For example, the components that make up the mesophase are mixed for about 1 minute to 1 week, preferably for 30 minutes to 5 days and most preferably 2 hours to 3 days, in order to form a mesophase which is ready for being further processed according to the invention.

According to another embodiment of the invention, a mesophase may be obtained by simply preparing a melt of the copolymer and optionally further components in the absence of an aqueous solution which is especially suited for prepolymers having a low melting or glass transition point.

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The mesophases of the invention comprise, for example, from 10 to 100 percent by weight of copolymer(s) of formula (1), from about 0 to about 90 percent by weight of aqueous solution and from 0 to 40 percent by weight of further components. Preferably, the bicontinuous mesophases of the invention comprise from about 30 to about 85 percent by weight of copolymer(s) of formula (1), from about 15 to about 70 percent by weight of aqueous solution and from 0 to 10 percent by weight of further components. Particularly preferred mesophases comprise from 30 to 75 percent by weight of copolymer(s) of formula (1) and from 25 to 70 percent by weight of aqueous solution.

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The solutions or mesophases comprising a block copolymer of formula (1) may be processed in a manner known *per se* to form moldings, especially contact lenses, for example by carrying out the photo-crosslinking of the copolymers of the invention in a suitable mold, in particular a contact lens mold. For example, the solution or mesophase is introduced into an ophthalmic mold in a manner known *per se*, such as, especially, by conventional metering in, for example by dropwise introduction or by extrusion. Suitable molds are generally customary contact lens molds as known in the state of the art. Thus, the contact lenses according to the invention can be manufactured, for example, in a manner known *per se*, for example in a conventional "spin-casting mold", as described, for example, in US-A-3 408 429, or by the so-called Full-Mould process in a static mold, as described, for example, in US-A-4347198. Appropriate molds are made, for example, from polypropylene. Quartz, sapphire glass and metals, for example, are suitable materials for re-usable molds.

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The crosslinking can be triggered in the mold, for example by actinic radiation, such as, for example, UV light, or by ionising radiation, such as, for example, gamma radiation, electron radiation or X radiation. The crosslinking can where appropriate also be triggered thermally or

electrochemically. Attention is drawn to the fact that the photocrosslinking can be carried out in a very short time, for example in ≤ 60 minutes, preferably ≤ 20 minutes, more preferably ≤ 5 minutes even more preferably in ≤ 1 minute, especially in up to 30 seconds, especially preferably, as disclosed in the examples.

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The opening of the mold such that the molding can be removed from the mold can be carried out in a manner known per se.

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The moldings obtainable from the block copolymers of formula (1) are preferably at least partly bicontinuous, that is to say the moldings, as stated before, have at least two partly bicontinuous phases, for example an oxygen-permeable and an ion-permeable phase, which are intermingled.

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The invention further relates, therefore, to moldings that comprise or, preferably, substantially consist of a crosslinked block copolymer of formula (1). Further examples of moldings of the invention, apart from contact lenses, are biomedical or special ophthalmic moldings, e.g. intraocular lenses, artificial cornea, eye dressings, moldings for use in surgery, such as heart valves, artificial arteries or the like, and films or membranes, e.g. membranes for controlling diffusion, photo-structurable films for information storage, or photoresist materials, e.g. membranes or moldings for etch resists or screen print resists.

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If the molding manufactured according to the invention is a contact lens and the latter has been manufactured under solventless conditions from a previously purified prepolymer of the invention, then it is normally unnecessary for the removal of the molding to be followed by purification steps, e.g. extraction, because the prepolymers used do not contain any undesired low-molecular-weight constituents; consequently, the crosslinked product also is free or substantially free of such constituents and subsequent extraction can be dispensed with. The contact lens can accordingly be converted into a ready-for-use contact lens directly in conventional manner by hydration. Suitable forms of hydration capable of producing ready-for-use contact lenses with a wide variety of water contents are known to the person skilled in the

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art. The contact lens is swelled, for example, in water, in an aqueous salt solution, especially in an aqueous salt solution having an osmolarity of approximately from 200 to 450 milliosmol in 1000 ml (unit: mosm/l), preferably approximately from 250 to 350 mosm/l and especially approximately 300 mosm/l, or in a mixture of water or an aqueous salt solution with a
 5 physiologically tolerable polar organic solvent, for example glycerol. Swelling of the prepolymer in water or in aqueous salt solutions is preferred.

The aqueous salt solutions used for the hydration are advantageously solutions of physiologically tolerable salts, such as buffer salts customary in the field of contact lens care, e.g. phosphate salts, or isotonicising agents customary in the field of contact lens care, such as, especially, alkali metal halides, e.g. sodium chloride, or solutions of mixtures thereof. An example of an especially suitable salt solution is a synthetic, preferably buffered, lachrymal fluid that has been matched to natural lachrymal fluid with regard to pH value and osmolarity, e.g. an unbuffered or preferably buffered, for example phosphate buffer-buffered, sodium chloride solution the osmolarity and pH value of which correspond to the osmolarity and pH value of
 10 human lachrymal fluid.

The hydration fluids defined above are preferably pure, that is to say free or substantially free of undesired constituents. Most preferably, the hydration fluid is pure water or a synthetic
 15 lachrymal fluid as described above.

If the molding manufactured according to the invention is a contact lens and the latter has been manufactured from an aqueous mesophase of a previously purified copolymer of the invention, the crosslinked product also will not contain any troublesome impurities. There is normally no
 20 need, therefore, for subsequent extraction. Since the crosslinking is carried out in an aqueous medium, there is also no need for subsequent hydration. In accordance with an advantageous embodiment, therefore, the contact lenses obtainable by this process are distinguished by the fact that they are suitable for use as intended without extraction or hydration. The expression "use as intended" is understood in this context to mean especially that the contact lenses can be
 25 inserted into the human eye.

The copolymers of the invention are especially suitable for the manufacture of mass-produced articles, such as, for example, contact lenses that are worn for a short time, for example for a month, a week or just one day, and are then replaced by new lenses. This is in particular
5 because contact lenses prepared from a mesophase of the copolymers can be used for their intended use without subsequent treatment steps, such as extraction or hydration. The copolymers of the invention are further useful for the manufacture of biomedical devices of all kinds, for example ophthalmic moldings such as intraocular lenses or artificial cornea, wound healing dressings, eye bandages, materials for the sustained release of an active compound such as a drug delivery patch, moldings that can be used in surgery, such as heart valves,
10 vascular grafts, catheters, artificial organs, encapsulated biologic implants, e.g. pancreatic islets, materials for prostheses such as bone substitutes, or moldings for diagnostics, membranes or biomedical instruments or apparatus.

In addition, biomedical devices, for example ophthalmic moldings such as in particular contact lenses obtainable according to the invention have a range of unusual and extremely advantageous properties and are therefore suited to extended periods of wear (true extended wear, i.e., seven days or more). Among these properties are, for example, their excellent compatibility with the human cornea and with tear fluid, which is based on a balanced ratio
15 between water content, oxygen permeability, ion permeability and mechanical and absorptive properties.

In particular, moldings obtainable from a block copolymer of the invention do have a high surface wettability which can be demonstrated by their contact angles, their water retention and
20 their water-film break up time or tear film break up time (TBUT).

The TBUT plays an particularly important role in the field of ophthalmic devices such as contact lenses. Thus the facile movement of an eyelid over a contact lens has proven important for the comfort of the wearer; this sliding motion is facilitated by the presence of a continuous layer of
25 tear fluid on the contact lens, a layer which lubricates the tissue/lens interface. An increased

wettability of the surface furthermore contributes substantially to low microbial adhesion and resistance to deposit formation.

The above outlined properties of the novel copolymers impart a high comfort and the absence of irritation and allergenic effects to biomedical moldings derived therefrom. Owing to their favourable permeability properties with respect to gases (CO_2 and O_2), various salts, nutrients, water and diverse other components of tear fluid, the contact lenses prepared according to the process of the invention have no effect, or virtually no effect, on the natural metabolic processes in the cornea. Furthermore, the contact lenses obtainable according to the process are optical clear and transparent, have a high shelf life and good mechanical properties, for example concerning the modulus of elasticity, elongation at break or dimensional stability.

All of the advantages mentioned above, in particular those concerning the surface wettability, apply to moldings derived from an amphiphilic block copolymer of the invention per se, that is to say without any subsequent surface treatment, e.g. coating. The block copolymers of the invention thus may be processed directly to biomedical moldings, in particular ophthalmic moldings, without any subsequent surface treatment, e.g. coating, whereas known polymeric materials in general have to be coated with an hydrophilic coating in order to be useful as a biomedical molding that comes in direct contact with the human body.

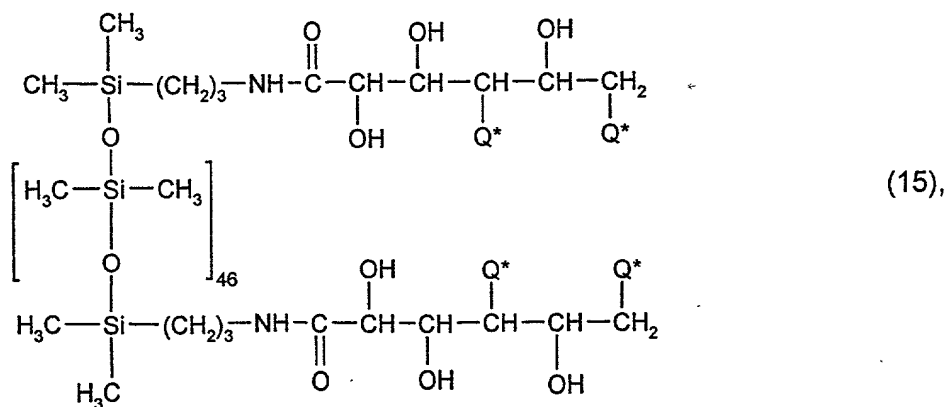
The above-mentioned advantages apply, of course, not only to ophthalmic moldings such as contact lenses but also to other moldings of the invention. The sum of the various advantageous aspects in the manufacture of the moldings of the invention results in the moldings of the invention being especially suitable as mass-produced articles, such as, for example, contact lenses that are worn for a short period and then replaced by new lenses.

In the Examples which follow, amounts are by weight, unless specified otherwise, and temperatures are given in degrees Celsius. Dynamic contact angle measurements are obtained using the dynamic Wilhelmy plate method, that is the wetting force on the solid is measured as the solid is immersed in or withdrawn from a liquid of known surface tension.

Example 1 :

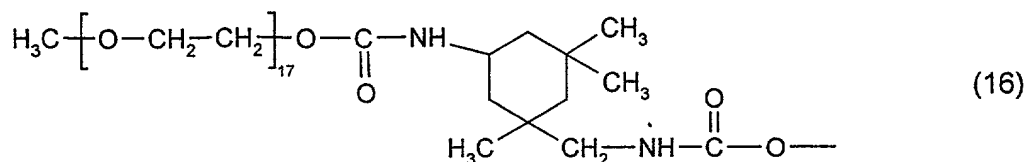
a) 11.8g (15.5 mmol) poly(ethyleneglycol) mono-methyl ether, M_n 750(PEG750) are dissolved in 13.8g anhydrous dichloroethane (DCE) in a round-bottomed flask. The PEG750 is dried by refluxing the water/DCE azeotrope through molecular sieves in a Soxhlet funnel. After drying, the contents of the flask is cooled, and 10.2g (45.8 mmol) isophoronediisocyanate (IPDI) are then added to the flask, along with 100 mg dibutyltin dilaurate (DBTDL). The contents are mixed overnight at room temperature. The solution is poured into a separatory funnel and the excess IPDI extracted with anhydrous hexane. The waxy-liquid PEG(750)-IPDI product is drained into a RBF and solvent removed under vacuum. The product is stored under vacuum over a weekend, then under nitrogen.

(b) In a three-necked round-bottomed flask are dissolved 8.0g (1.4 mmol) of the compound of formula



wherein Q^* is a radical $-\text{O}-\text{C}(\text{O})-\text{NH}-(\text{CH}_2)_2-\text{O}-\text{C}(\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$ (synthesis see PCT application WO 96/36890) in 30g anhydrous dichloroethane. To this solution are added 4.1g (4.1 mmol) of the PEG(750)-IPDI. The flask is equipped with a condenser, a thermometer, stir bar, and heating mantle. The mixture is stirred and heated to 45°C. DBTDL catalyst is added, and dry air is infused through the system. After 7 days, no isocyanate peak is visible in the IR, and the solution is then cooled. The solvent is removed via rotary evaporation to yield 10.2g of a

product corresponding to the above formula (15), wherein 3 hydroxy groups have been substituted by a radical of formula

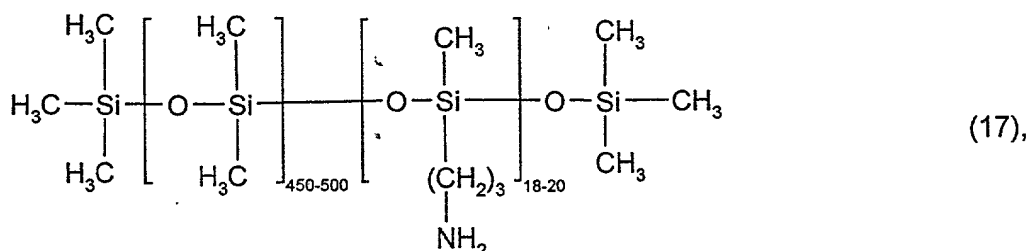


c) 0.8109g of the product obtained according to step b) are mixed with 0.2g water containing 0.01% of a photoinitiator (Darocur® 2959). This mixture is centrifuged, refrigerated overnight, mixed, and recentrifuged until the formulation looks homogeneous and transparent. This formulation is cast on quartz plates that had been soaked overnight in KOH/isopropanol,, rinsed with ethanol, then rinsed with purified water and air dried. The films are cured for 90 seconds under a UV lamp, and extracted with an isopropanol/water mixture. Dynamic contact angle measurements are obtained which indicate a high surface wettability of the films.

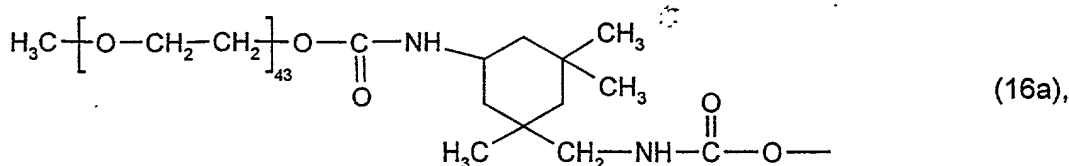
Example 2 :

a) 15.0g (7.8 mol) poly(ethyleneglycol) mono-methyl ether, M_n 1900 (PEG1900) is dissolved in 20g anhydrous dichloromethane in a round-bottomed flask. The PEG1900 is dried by refluxing the water/ dichloromethane azeotrope through molecular sieves in a Soxhlet funnel. After drying, the contents of the flask are cooled, and 5.3g (24.0 mmol) isophoronediiisocyanate (IPDI) are added to the flask, along with 100 mg dibutyltin dilaurate (DBTDL). The contents are mixed over the weekend at room temperature. The solution is poured into a separatory funnel and the excess IPDI extracted with anhydrous hexane. The PEG-IPDI product is drained into a RBF and solvent removed under vacuum. The product is stored under vacuum.

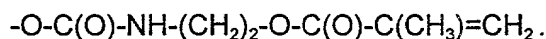
b) In a round-bottomed flask are dissolved 5.03g (0.13 mmol) of a compound of formula



in 10.4g anhydrous dichloroethane (DCE). To this solution are added 1.9g (1.9 mmol) of the PEG(1900)-IPDI product according to step a) dissolved in 10.2g anhydrous DCE. The mixture is stirred at room temperature under nitrogen for 3.5 hours. Then 0.26g (1.7 mmol) of isocyanatoethyl methacrylate are added to the mixture, which is stirred under infused dry air a few hours, until the isocyanate peak is no longer visible in the IR. The solvent is then removed via rotary evaporation to yield a product of the above formula (17), wherein about 35 % of the amino groups are substituted by a radical of formula



and the remaining amino groups are substituted by a radical



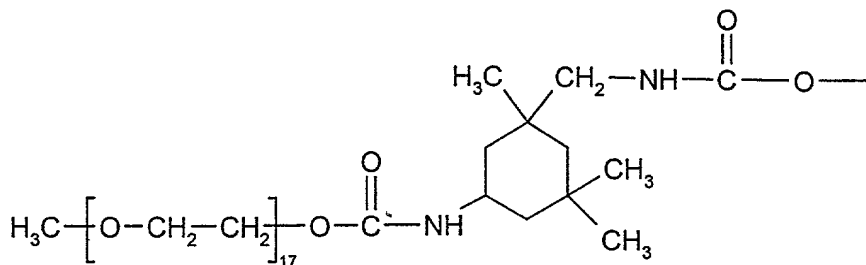
c) 1.51g of the product obtained according to step b) are mixed with 1.51g ethanol and 7.5 mg of a photoinitiator (Darocur® 1173). This mixture is stirred to dissolve, degassed, and cast in a dry box on quartz plates that has been soaked overnight in KOH/isopropanol,, rinsed with ethanol, then rinsed with purified water and air dried. The flats are cured for 15 minutes under a UV lamp, and extracted with an isopropanol/water mixture. Dynamic contact angle measurements are obtained which indicate a high surface wettability of the flats.

Example 3 :

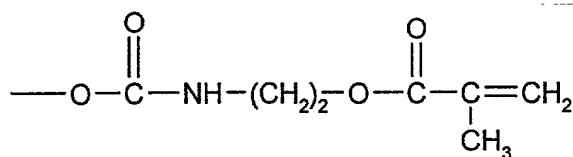
(a) 11.8g (15.5 mmol) poly(ethyleneglycol) mono-methyl ether (PEG750) are dissolved in 13.8g anhydrous dichloroethane (DCE) in a round-bottomed flask. The PEG750 is dried by refluxing the water/DCE azeotrope through molecular sieves in a Soxhlet funnel. After drying, the contents of the flask are cooled, and 10.2g (45.8 mmol) isophoronediiisocyanate (IPDI) are added to the flask, along with 100 mg dibutyltin dilaurate (DBTDL). The contents are mixed overnight at room temperature. The solution is poured into a separatory funnel and the excess IPDI extracted with anhydrous hexane. The waxy-liquid PEG(750)-IPDI product is drained into a RBF and solvent removed under vacuum. The product is stored under vacuum over a weekend, then under nitrogen.

b) To a three-necked round-bottomed flask are added 0.87g (4.88 mmol) D(+) gluconic acid- δ -lactone, and 21 ml anhydrous tetrahydrofuran. The flask is equipped with a condenser, a thermometer, stir bar, and heating mantle. An addition funnel containing 10.00g (0.26 mmol) of the compound of formula (17) according to Example 2 is also attached, and dry nitrogen is infused through the system. The contents of the flask are heated to 38°C. The solution of the compound of formula (17) is added dropwise to the stirring gluconolactone solution. The reaction is stirred at 38°C overnight. The mixture is then cooled and stirred at room temperature over the weekend. The solvent is removed under vacuum. There are obtained 10.59g of a product according to formula (17) wherein the amino groups are each substituted by a radical of formula -NH-C(O)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH₂-OH.

c) 4.00g (0.094 mmol) of the product obtained according to step (b) are weighted into a three-necked round-bottomed flask, along with 25.59g tetrahydrofuran. Next, 1.30g (1.32 mmol) PEG(750)-IPDI obtained according to step a) and 0.07g (0.45 mmol) isocyanatoethyl methacrylate are added to the flask, and the mixture stirred. The flask is placed atop a stir plate and equipped with heating mantle, condenser, and thermometer. Dry air is infused through the system. The reactants are brought to 41°C, and 100 mg dibutyltin dilaurate are added to the reaction mixture. The mixture is stirred at 41°C over the weekend. The mixture is then cooled and the solvent removed under reduced pressure. 5.30g of a clear, crystalline compound corresponding to formula (17) wherein the amino groups are each substituted by a radical of formula -NH-C(O)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH₂-OH and about 13 % of the hydroxy groups are substituted by a radical of formula



and about 4 % of the hydroxy groups are substituted by a radical of formula

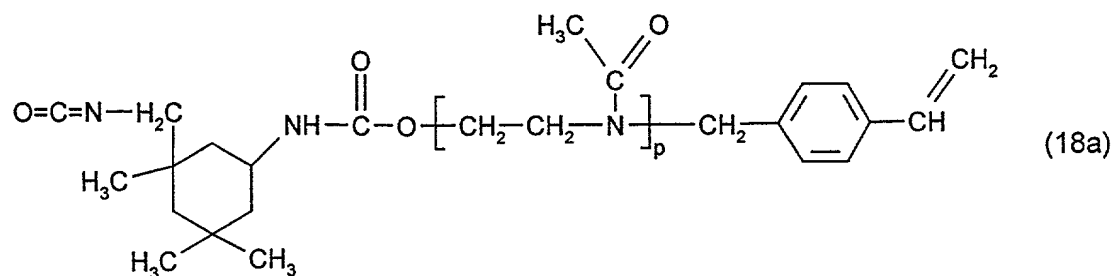


are recovered.

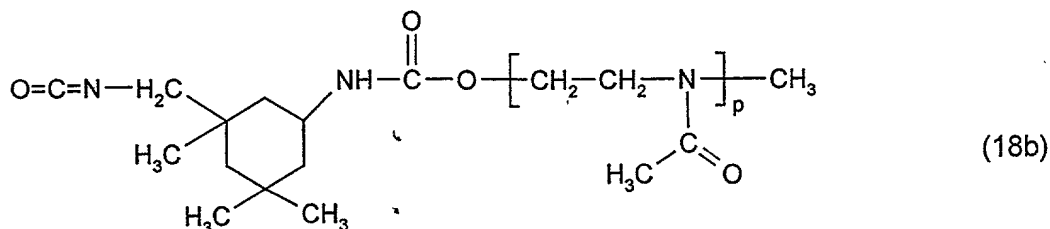
d) 1.1g of the product obtained according to step c) are mixed with 1.1g ethanol and 9.4mg of a photoinitiator (Darocur® 1173). This formulation is cast on quartz plates that have been soaked overnight in KOH/isopropanol,, rinsed with ethanol, then rinsed with purified water and air dried. The films are cured for 90 seconds under a UV lamp, and extracted with an isopropanol/water mixture. Dynamic contact angle measurements are obtained which indicate a high wettability of the films obtained.

Example 4:

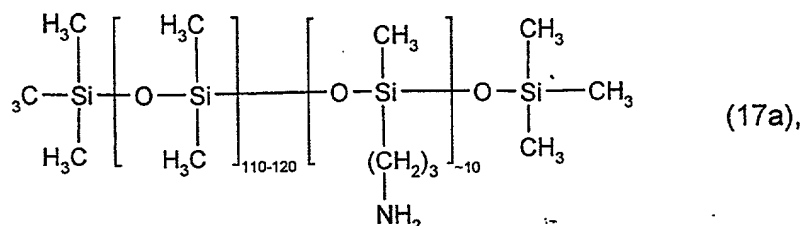
A 50 ml addition funnel containing 1.0g of the compound of formula



($M_w \sim 1500$, synthesis from $\text{HO---(CH}_2\text{CH}_2\text{N[C(O)CH}_3\text{)]}_p\text{---CH}_2\text{---C}_6\text{H}_5\text{---CH=CH}_2$) prepared according to S. Kobayashi et al., Polymer Bulletin 13, p 447-451 (1985) and isophorone diisocyanate) and 1.0g of the compound of formula



($M_w \sim 1300$, synthesis from isophorone diisocyanate and $\text{HO}-(\text{CH}_2\text{CH}_2\text{N}[\text{C}(\text{O})\text{CH}_3])_p-\text{CH}_3$ in 10.1g dry methylene chloride is placed atop a 100 ml round-bottomed flask, equipped with a stir bar and containing 3.0g of the distilled compound of formula



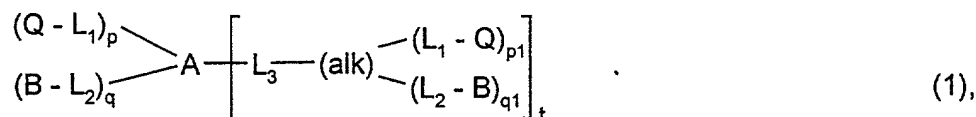
M_w about 10000, and 10.2g dry methylene chloride. The flask is placed atop a stir plate, and a septum placed in the add-funnel neck. Stirring is started and addition of the polymethyl oxazoline materials starts. The addition takes 40 minutes, after which the mixture is stirred an additional 4 hours at room temperature. One drop of DBTDL is added to the reaction mixture, which is stirred an additional hour. The solvent is then removed via rotary evaporation.

The macromer obtained above is formulated 68.62% in water containing 0.5% of a photoinitiator (Irgacure® 2959). It is centrifuged and stirred. The formulation is cast on quartz plates, and cured for 60 seconds. Thereafter the flats are peeled off the quartz plates, placed in water and autoclaved. Dynamic contact angle measurements are obtained which indicate a high wettability of the films obtained.

Comparative Example: The manufacture of the molding above is repeated but using 2g of the compound of formula (18a) instead of the mixture of 1g each of a compound of formula (18a) and (18b). Dynamic contact angle measurements are obtained which indicate a considerable decrease in wettability compared to the molding obtained with the mixture of compounds (18a) and (18b).

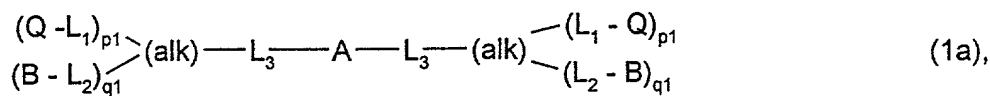
What is claimed is:

1. An amphiphilic block copolymer of formula



- 5 wherein A is a hydrophobic polysiloxane or perfluoroalkyl polyether segment;
 B is a surface-modifying hydrophilic segment having a weight average molecular weight of ≥ 100
 that is devoid of a crosslinkable group;
 Q is a moiety comprising at least one crosslinkable ethylenically unsaturated group;
 (alk) is C_2 - C_{20} -alkylene which is unsubstituted or substituted by hydroxy;
 10 L_1 , L_2 and L_3 are each independently of the other a linking group;
 $p1$ and $q1$ are each independently of the other an integer from 1 to 12; and either
 t is 0 and p and q are each independently of the other an integer from 1 to 25; or
 t is an integer from 1 to 8 and p and q are each 0.

15 2. An amphiphilic block copolymer according to claim 1 of formula



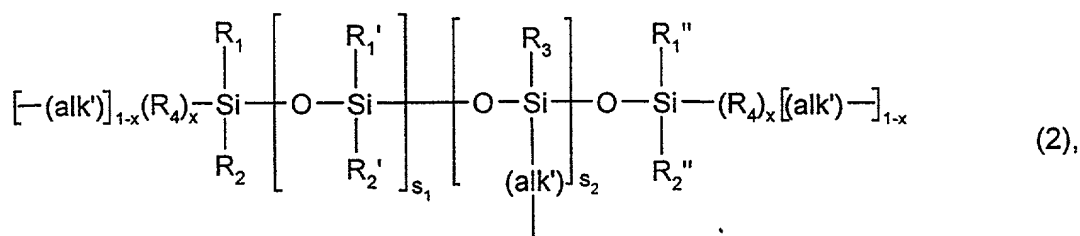
wherein A, B, L_1 , L_2 , L_3 , Q, (alk), $p1$ and $q1$ are each as defined in claim 1.

3. An amphiphilic block copolymer according to claim 1 of formula



wherein A, B, L_1 , L_2 and Q are each as defined in claim 1, and p and q are each independently
 of the other an integer from 2 to 20.

25 4. An amphiphilic block copolymer according to claim 1, wherein A is a polysiloxane segment of
 formula



wherein (alk') is alkylene having 1 to 20 carbon atoms which may be interrupted by -O-;

x is 0 or 1;

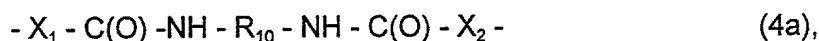
80 to 100 % of the radicals R_1 , R_1' , R_1'' , R_2 , R_2' , R_2'' , R_3 and R_4 , independently of one another, are C_1 - C_8 -alkyl, and 0-20% of the radicals R_1 , R_1' , R_1'' , R_2 , R_2' , R_2'' , R_3 and R_4 , independently of one another, are unsubstituted or C_1 - C_4 alkyl- or C_1 - C_4 -alkoxy-substituted phenyl, fluoro(C_1 - C_{18} -alkyl) or cyano(C_1 - C_{12} -alkyl),

s_1 is an integer from 5 to 700;

s_2 is the sum of (p+q+t-2) if x is 0, and is the sum of (p+q+t) if x is 1; wherein p, q and t are as defined in claim 1, and

the sum (s_1+s_2) is from 5 to 700.

5. An amphiphilic block copolymer according to claim 1, wherein L_1 , L_2 and L_3 are each independently of the other a bivalent linking group of formula



wherein X_1 and X_2 are each independently of the other a group -O-, -S- or -NR₀-, R₀ is hydrogen or C_1 - C_4 -alkyl, and R_{10} is linear or branched C_1 - C_{18} -alkylene or unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_6 - C_{10} -arylene, C_7 - C_{18} -aralkylene, C_6 - C_{10} -arylene- C_1 - C_2 -alkylene- C_6 - C_{10} -arylene, C_3 - C_8 -cycloalkylene, C_3 - C_8 -cycloalkylene- C_1 - C_6 -alkylene, C_3 - C_8 -cycloalkylene- C_1 - C_2 -alkylene- C_3 - C_8 -cycloalkylene or C_1 - C_6 -alkylene- C_3 - C_8 -cycloalkylene- C_1 - C_6 -alkylene.

6. An amphiphilic block copolymer according to claim 5, wherein L_1 is a linking group of formula (4a), (4c) or (4e), L_2 is a linking group of formula (4a), and L_3 is a linking group of formula (4b) or (4c).

5 7. An amphiphilic block copolymer according to claim 1, wherein B is a non-ionic segment selected from the group consisting of a polyoxyalkylene, polysaccharid, polypeptide, poly(vinylpyrrolidone), polyalkylacrylate or -methacrylate, polyhydroxyalkylacrylate or -methacrylate, polyacyl alkylene imine, polyacryl amide, polyvinyl alcohol, polyvinyl ether and a polyol, or is a polyionic segment selected from the group consisting of a polyallylammonium, polyethylenimine, polyvinylbenzyltrimethylammonium, polyaniline, sulfonated polyaniline, polypyrrole and polypyridinium segment, and a polyacrylic and polymethacrylic acid, a polythiophene-acetic acid, a polystyrenesulfonic acid and a zwitterionic segment, or a suitable salt thereof.

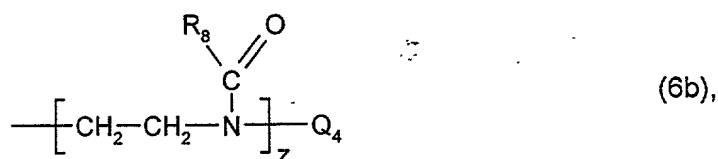
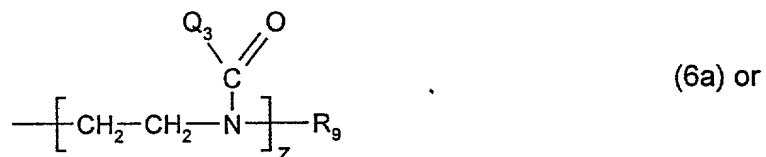
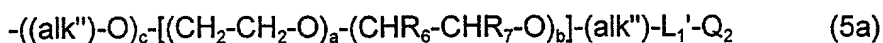
10 8. An amphiphilic block copolymer according to claim 1, wherein Q is a radical Q_1 of formula



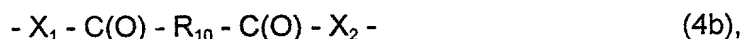
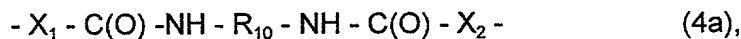
wherein (Alk) is linear or branched C_1 - C_{12} -alkylene, X is -O- or -NH-, R_{11} is an olefinically unsaturated copolymerisable radical having from 2 to 24 carbon atoms which is unsubstituted or further substituted by C_1 - C_4 alkoxy, halogen, phenyl or carboxy, and w is the number 0 or 1.

20 9. An amphiphilic block copolymer according to claim 1, wherein Q is a polyoxyalkylene, poly(vinylpyrrolidone), poly(hydroxyethylacrylate), poly(hydroxyethylmethacrylate), polyacrylamide, poly(N,N-dimethylacrylamide), polyacrylic acid, polymethacrylic acid, polyacyl alkylene imine or a copolymeric mixture of two or more of the above-mentioned polymers which
25 in each case comprises one or more ethylenically unsaturated bond and has a weight average molecular weight of, for example, ≥ 100 .

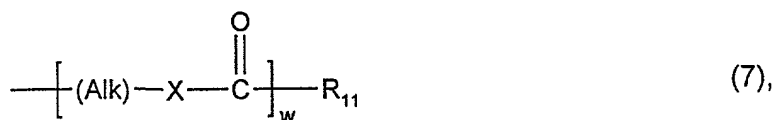
10. An amphiphilic block copolymer according to claim 9, wherein Q is a hydrophilic segment of formula



wherein L_1' is a bivalent linking group of formula



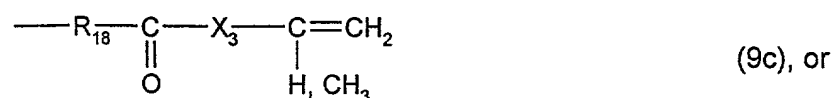
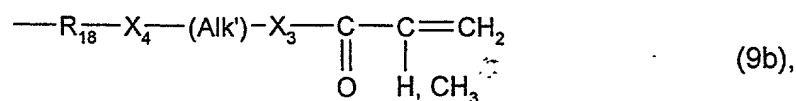
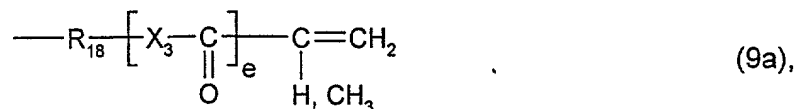
wherein X_1 and X_2 are each independently of the other a group $-\text{O}-$, $-\text{S}-$ or $-\text{NR}_0-$, R_0 is hydrogen or C_1 - C_4 -alkyl, and R_{10} is linear or branched C_1 - C_{18} -alkylene or unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_6 - C_{10} -arylene, C_7 - C_{18} -aralkylene, C_6 - C_{10} -arylene- C_1 - C_2 -alkylene- C_6 - C_{10} -arylene, C_3 - C_8 -cycloalkylene, C_3 - C_8 -cycloalkylene- C_1 - C_6 -alkylene, C_3 - C_8 -cycloalkylene- C_1 - C_2 -alkylene- C_3 - C_8 -cycloalkylene or C_1 - C_6 -alkylene- C_3 - C_8 -cycloalkylene- C_1 - C_6 -alkylene, Q_2 is a radical of formula



wherein (Alk) is linear or branched C_1 - C_{12} -alkylene, X is $-\text{O}-$ or $-\text{NH}-$, R_{11} is an olefinically unsaturated copolymerisable radical having from 2 to 24 carbon atoms which is unsubstituted or further substituted by C_1 - C_4 alkoxy, halogen, phenyl or carboxy, and w is the number 0 or 1,

Q₃ is C₃-C₁₂-alkenyl or a radical -(CH₂)₁₋₄-O-R₁₆ wherein R₁₆ is acryloyl, methacryloyl or a group -C(O)-NH-(CH₂)₂₋₄-O-C(O)-C(R₁₇)=CH₂ and R₁₇ is hydrogen or methyl,

Q₄ is a radical of formula



wherein X₃ is -O- or -NR, R is hydrogen or C₁-C₄-alkyl, X₄ is a group -C(O)-O-, -O-C(O)-NH- or -NH-C(O)-O-, (Alk') is C₁-C₈-alkylene, e is an integer of 0 or 1, and R₁₈ is C₁-C₁₂-alkylene, phenylene or C₇-C₁₂-phenylenealkylene,

one of the radicals R₆ and R₇ is hydrogen and the other is methyl,

(alk'') is C₁-C₆-alkylene, c is the number 0 or 1, and each of a and b independently of the other is a number from 0 to 100, the sum of (a+b) being from 2 to 100,

R₈ is hydrogen; C₁-C₁₂-alkyl unsubstituted or substituted by hydroxy or fluoro and/or

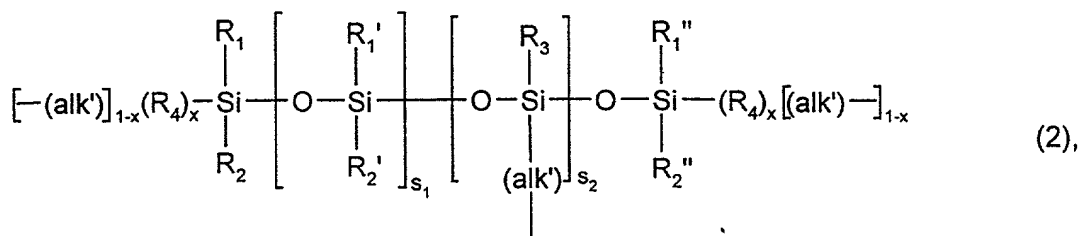
uninterrupted or interrupted by oxygen; C₅-C₈-cycloalkyl; phenyl; or benzyl,

R₉ is C₁-C₁₂-alkyl, benzyl, C₂-C₄-alkanoyl, benzoyl or phenyl, and

z is an integer from 2 to 150.

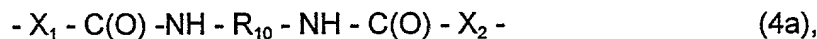
11. An amphiphilic block copolymer according to claim 2 of formula (1a), wherein

A is a polysiloxane segment of formula



wherein x and s_2 are each 0, and $R_1, R_1', R_1'', R_2, R_2', R_2'', R_3$ and R_4 are each independently of one another C_1 - C_4 -alkyl, B is a polyoxyalkylene, poly(vinylpyrrolidone), poly(hydroxyethylacrylate), poly(hydroxyethylmethacrylate), polyacrylamide, poly(N,N -dimethylacrylamide), polyacrylic acid, polymethacrylic acid, polyacyl alkylene imine or a copolymeric mixture of two or more of the above-mentioned polymers,

L_1 is a linking group of formula



L_2 is a linking group of the above formula (4a), and L_3 is a linking group of the above formula (4c) or of the formula



wherein X_1 and X_2 are each independently of the other a group $-O-$, $-S-$ or $-NR_0-$, R_0 is hydrogen or C_1 - C_4 -alkyl, and R_{10} is linear or branched C_1 - C_{18} -alkylene or unsubstituted or C_1 - C_4 -alkyl- or C_1 - C_4 -alkoxy-substituted C_6 - C_{10} -arylene, C_7 - C_{18} -aralkylene, C_6 - C_{10} -arylene- C_1 - C_2 -alkylene- C_6 - C_{10} -arylene, C_3 - C_8 -cycloalkylene, C_3 - C_8 -cycloalkylene- C_1 - C_6 -alkylene, C_3 - C_8 -cycloalkylene- C_1 - C_2 -alkylene- C_3 - C_8 -cycloalkylene or C_1 - C_6 -alkylene- C_3 - C_8 -cycloalkylene- C_1 - C_6 -alkylene,

Q is a radical Q_1 of formula



wherein (Alk) is linear or branched C_1 - C_{12} -alkylene, X is $-O-$ or $-NH-$, R_{11} is an olefinically unsaturated copolymerisable radical having from 2 to 24 carbon atoms which is unsubstituted or further substituted by C_1 - C_4 alkoxy, halogen, phenyl or carboxy, and w is the number 0 or 1, or Q

is a polyoxyalkylene, poly(vinylpyrrolidone), poly(hydroxyethylacrylate), poly(hydroxyethylmethacrylate), polyacrylamide, poly(N,N-dimethylacrylamide), polyacrylic acid, polymethacrylic acid, polyacyl alkylene imine or a copolymeric mixture of two or more of the above-mentioned polymers which in each case comprises one or more ethylenically unsaturated bond and has a weight average molecular weight of, for example, ≥ 100 , and p1 is an integer from 1 to 6, and q1 is an integer from 1 to 8.

12. An amphiphilic block copolymer according to claim 3 of formula (1b), wherein A, B, L₁, L₂ and Q are as defined in claim 11, and p and q are each independently of the other an integer 2 to 15.

13. A process for the manufacture of a molding, which comprises crosslinking an amphiphilic block copolymer of formula (1) according to claim 1 in a mold.

14. A process according to claim 13 wherein the molding is an ophthalmic molding and wherein the block copolymer is photo-crosslinked in an ophthalmic mold using actinic radiation.

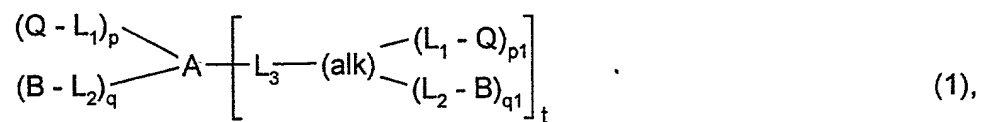
15. A molding obtained by the process according to claim 13.

16. A molding according to claim 15, which is an ophthalmic molding, intraocular lens, or artificial cornea.

17. A molding according to claim 15, which is a contact lens.

Abstract

The invention relates to novel crosslinkable copolymers of formula



- 5 wherein the variables are as defined in the claims. The copolymers of the invention are especially useful for the manufacture of biomedical moldings, for example ophthalmic moldings such as in particular contact lenses.

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,
and

I believe I am an original, first and joint inventor of the subject matter which is claimed
and for which a patent is sought on the invention entitled
Organic Compounds
the specification of which is attached hereto.

I hereby state that I have reviewed and understand the contents of the above identified
specification, including the claims.

I acknowledge my duty to disclose all information which is known by me to be material to
the patentability of this application as defined in 37 C.F.R. §1.56.

I hereby claim the benefit under 35 U.S.C. §119(a)-(d) or §365(b) of any foreign
application(s) for patent or inventor's certificate listed below and under 35 U.S.C. §365(a) of any
PCT international application(s) designating at least one country other than the United States
listed below and have also listed below any foreign application(s) for patent or inventor's
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United States for the same subject matter and having a filing date before that of the application
the priority of which is claimed for that subject matter:

None

I hereby claim the benefit under 35 USC §119(e) of any United States provisional
application(s) listed below:

Application No.

Filing Date

March 30, 1999*

*Note: The case was converted to a provisional application from patent application Serial
No. 09/280,510 on March 14, 2000.

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) listed below and under 35 U.S.C. §365(c) of any PCT international application(s) designating the United States listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in said prior application(s) in the manner required by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose all information known by me to be material to patentability as defined in 37 C.F.R. §1.56 which became available between the filing date(s) of the prior application(s) and the national or PCT international filing date of this application:

None

I hereby appoint the attorneys and agents associated with Customer No. 001095, respectively and individually, as my attorneys and agents, with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. §1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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